

Reverse Micelles Enable Strong Electrostatic Interactions of Colloidal Particles in Nonpolar Solvents

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While the important role of electrostatic interactions in aqueous colloidal suspensions is widely known and reasonably well-understood, the relevance of charge in nonpolar suspensions remains mysterious. We demonstrate that particles can have surprisingly strong electrostatic interactions in low dielectric constant environments when ions are solubilized by reverse micelles. A simple thermodynamic model, relating the structure of the micelles to the equilibrium ionic strength, is in good agreement with both conductivity and interaction measurements. Since dissociated ions are solubilized by reverse micelles, the entropic incentive to charge a particle surface is qualitatively changed, and surface entropy plays an important role.

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Charge is a powerful tool for manipulating the properties of complex fluids. In aqueous colloids, charges readily dissociate and play an essential role in determining the structure of suspensions and their response to electrical, mechanical and optical stimuli. Perhaps most importantly, charge stabilizes aqueous colloidal particles against flocculation. By contrast, charge is commonly thought to play no role in nonpolar environments in thermodynamic equilibrium. However, a close examination of existing technologies suggests a richer story. Most stunningly, by assigning opposite charges to absorbing and reflecting particles, nonpolar suspensions have been engineered to act as electrophoretic ink [1]. Furthermore, charge control agents have long been added to petroleum products to reduce the risk of explosions during processing and transport [2]. There is even some evidence that charge contributes to the stability of soot in diesel engine oil [3]. In these cases, reverse micelles play a crucial role by reducing the electrostatic penalty of ionization and thereby stabilizing ions in equilibrium [4]. In all cases, it is absolutely essential that ions are made soluble in this low dielectric constant environment. Recently, force measurements have provided the first direct evidence of electrostatic repulsions between charged surfaces in a nonpolar solvent [5, 6]. Despite the growing acknowledgement of the importance of charge in nonpolar systems, a useful quantitative framework to describe the origin and interactions of charge, comparable to the theory of Derjaguin-Landau-Verwey and Overbeek (DLVO) for aqueous systems [7, 8], does not exist. Such an understanding is essential to fully exploit the technological capabilities of charge in nonpolar solvents and to fully comprehend the behavior of these fascinating systems

In this Letter, we present a physical picture of the origins of charge and the interactions of colloidal particles in nonpolar solvents with reverse micelles. Our experiments show that particles charge and interact strongly with screened-Coulomb interactions. Ions reside within the polar cores of reverse micelles. Reverse micelles not only

stabilize charge dissociated from particle surfaces, but also charge spontaneously to provide additional screening of electrostatic interactions. The confinement of charge within reverse micelles qualitatively changes the entropic incentive to charging: the configurational entropy of the particle surface charge, typically negligible in aqueous systems, plays a critical role.

We explore the interactions of colloidal PMMA particles suspended in a mixture of oil and surfactant. The particles have a radius of 780 nm and are sterically-stabilized by a layer of poly(12-hydroxy-steric-acid) (PHSA) hairs grafted to their surface. The particles are suspended in a mixture of dodecane and an ionic surfactant, di-2-ethylhexylsulfosuccinate (AOT). Above its critical micellar concentration, AOT forms reverse micelles whose size is very nearly independent of concentration, [9, 10]. These micelles are very hygroscopic. To minimize the effects of moisture, we mix pure dodecane (99%) and AOT (98%) in a dry glovebox. All measurements are either performed in the glovebox or with sample cells that have been sealed in the glovebox.

In pure dodecane, our PMMA particles reversibly aggregate, as shown in Fig. 1(a). However, when AOT is added at concentrations above its critical micellar concentration, the particles disperse. Moreover, particles in suspensions with 12 mM AOT rarely approach within three particle diameters in each other, as shown in Fig. 1(b). We quantify this surprisingly strong repulsion by collecting a series of statistically independent images of a freely-diffusing monolayer of particles confined between two microscope slides. The centers of each particle are then precisely located [11] to calculate the ensemble-averaged two-point density correlation function, $g(r)$, using a total of about 40,000 particles. As shown in the inset of Fig. 1(c), particles in a 12 mM suspension never come within four microns of each other. At larger separations, $g(r)$ rises slowly to a peak near $7\text{ }\mu\text{m}$ and decays to unity at larger separations. In order to minimize the effect of the confining surfaces, the surfaces of the sam-

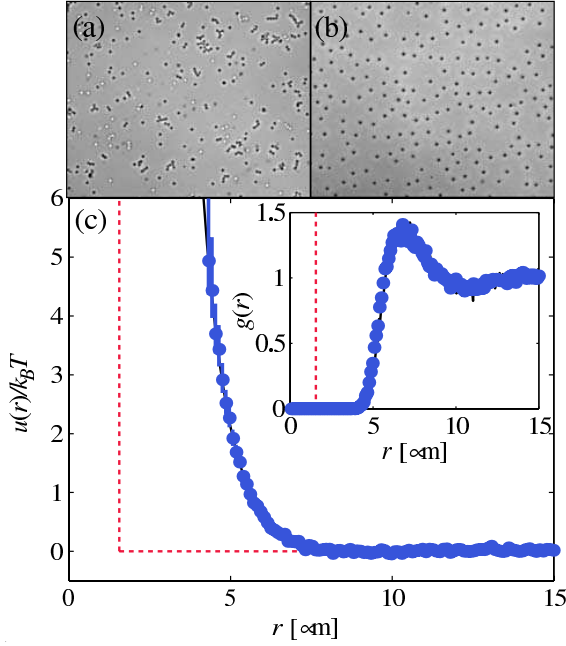


FIG. 1: Charge-stabilization of a nonpolar suspension. (a) Optical micrographs of PMMA particles in pure dodecane and (b) with 12mM AOT, field of view $135 \times 108 \mu\text{m}^2$. (c) Inferred particle pair potential, symbols, and fit to screened-Coulomb interaction, line. For comparison, a hard sphere interaction is plotted as a dashed line. Inset. Measured and simulated equilibrium pair correlation functions, symbols and line, respectively. A dashed line indicates contact.

ple cell are prepared to mimic the surface of the particles and interactions are measured in the thickest regions of the cell that contain a well-confined monolayer [19]

The observed pair-correlation function is consistent with the repulsive component of the DLVO theory of colloidal interactions. We extract pair potentials by inverting $g(r)$ with liquid structure theory [12]. Using the resulting potentials, 2-D Monte Carlo simulations of our experiments generate pair-correlation functions that are in good agreement with those measured. A comparison of measured and simulated $g(r)$'s for a sample with 12 mM AOT is shown in the inset of Fig. 1(c), where data and simulation are indistinguishable. The observed potential, shown in Fig. 1(c), is in excellent agreement with the screened-Coulomb form,

$$\frac{u(r)}{k_B T} = \left(\frac{e\zeta}{k_B T} \right)^2 \frac{a^2}{\lambda_B} \frac{e^{-\kappa(r-2a)}}{r}, \quad (1)$$

where ζ is the apparent potential at the surface of the particle. The Debye length, $\kappa^{-1} = 1/\sqrt{4\pi\lambda_B n_{ion}}$, characterizes the range of electrostatic interactions, where n_{ion} is the number density of ions. The Bjerrum length, $\lambda_B = e^2/4\pi\epsilon\epsilon_0 k_B T$, is the separation of two elementary charges when their electrostatic interaction energy is equal to $k_B T$. A least-squares fit to our data yields $e|\zeta|/k_B T = 4.4 \pm 0.3$ and $\kappa = (1.07 \pm 0.05) \mu\text{m}^{-1}$. Defy-

ing conventional wisdom, this zeta potential is as high as those found in highly-charged aqueous systems [13, 14]. However, the effective charge,

$$Z = \zeta(a/\lambda_B)(1 + \kappa a), \quad (2)$$

is 225 ± 15 , two orders of magnitude below that measured in similarly sized charged particles in water. This charge on the surface of particles must be balanced by counterions in solution to ensure charge neutrality. Using our measured value of Z and the number density of particles, we calculate the density of counterions to be about $0.5 \mu\text{m}^{-3}$. However, this ion density is too low to account for the observed value of κ , which implies a significantly larger ion density of $3.3 \pm 0.3 \mu\text{m}^{-3}$. Therefore, particle surfaces must not be the only source of stable ions in solution.

Indeed, stable ions exist in solutions of AOT in dodecane without particles. While these ions are too small to be imaged optically, we can detect their presence through their contribution to solution conductivity. Assuming that charge is carried by singly charged micelles, then the conductivity

$$\sigma = \frac{e^2 n_{ion}}{6\pi\eta a_h}, \quad (3)$$

where a_h is the hydrodynamic radius of the micelles and η is the solvent viscosity. Our 12 mM AOT solutions have a conductivity of 17 pS/cm. Using the known hydrodynamic radius of AOT reverse micelles in dodecane, we find an ion density of $2.7 \pm 0.4 \mu\text{m}^{-3}$, consistent with $\kappa = 0.98 \pm 0.05 \mu\text{m}^{-1}$, in good agreement with our interaction measurements. Therefore, ambient charged micelles dominate the ionic strength of the system. However, by comparing the number density of ions to the number density of micelles, calculated from AOT concentration and micellar aggregation number, we find that only one micelle in 10^5 develops a charge.

To elucidate the origin of this excess charge, we measure the scaling of solution conductivity with AOT concentration. Varying the concentration of AOT from 0.8 to 200 mM, the conductivity increases linearly from 1 to 500 pS/cm, as shown in Fig. 2. Therefore, the ratio of ions to micelles, $\chi = n_{ion}/n_{micelle}$ is independent of the concentration of AOT, and $\chi = 1.2 \times 10^{-5}$. Only a tiny fraction of micelles ionize to form a charge carrier. While weak electrolytes, of the form $AB \rightleftharpoons A^+ + B^-$, can exhibit similar ionization fractions, χ would scale like $[AB]^{-1/2}$. Instead, a charging mechanism where neutral micelles reversibly exchange charge through a collision, $A + A \rightleftharpoons A^+ + A^-$, leads, through the law of mass action, to a ionization fraction independent of the concentration of A [4, 15], as demanded by our data. The fraction of charged micelles is determined by the difference in free energy between the charged and uncharged states, $\chi = 2 \exp(-\Delta F/2k_B T)$. If the free-energy cost of ionizing a single isolated micelle is g_M ,

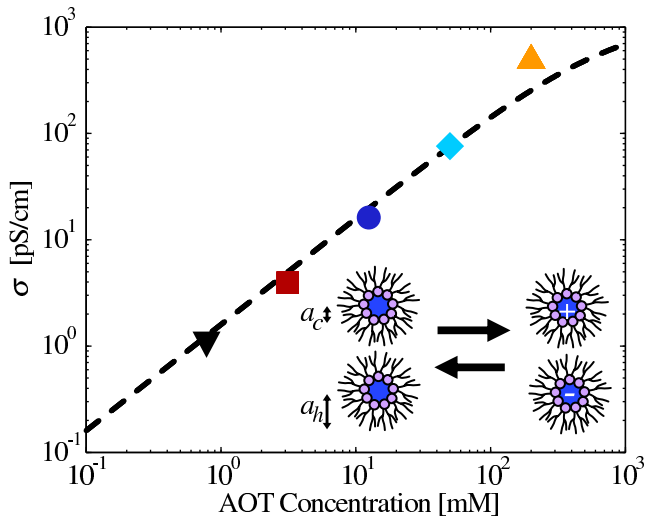


FIG. 2: Conductivity of AOT/dodecane solutions without particles. Symbols indicate measurements, and dashed curve indicates fit to Eq. 3 with empirical [AOT]-dependent solution viscosity. *inset* Schematic diagram of two-body process that leads to the creation of charge in the bulk of the solution.

then $\chi = 2 \exp(-g_M/k_B T)$. Comparing this basic thermodynamic result to our measured value of χ , we find that $g_M = 12 k_B T$.

The measured micelle ionization energy has a simple electrostatic interpretation. A singly-charged conducting sphere of radius a_c surrounded by a dielectric medium has a electrostatic energy $\lambda_B/2a_c$ [16]. Assuming that electrostatic contributions dominate the ionization free-energy and the core of the micelle is effectively a conductor, then our measured value of g_M implies a core radius, $a_c = 1.2$ nm. This is in good agreement with neutron scattering measurements [17]. Thus, we conclude that the equilibrium ionic strength of a solution of reverse micelles is determined by a competition between entropy and electrostatics. The relative size of the Bjerrum length and the micellar core radius determine the charge fraction. When $\lambda_B \gg a_c$ a small fraction of micelles charge. When $\lambda_B \approx a_c$, nearly all of the micelles can charge and individual micelles can become multiply-charged.

Ionic strength has a dramatic effect on the interactions between particles. We find that the range of the interactions is greatly reduced as the concentration of AOT increases from 3 to 200 mM, as shown in Fig. 3. At the lowest concentration of AOT, particles feel a repulsion greater than $k_B T$ at center-to-center separations less than $7 \mu\text{m}$ or 4.5 particle diameters. At the highest concentration, particles can approach each other within $2.5 \mu\text{m}$. These data are all fit by the DLVO form with a constant apparent surface potential $e|\zeta|/k_B T = 4.1 \pm 0.1$ and κ^{-1} ranging from 0.2 to $1.4 \mu\text{m}$. The ionic strengths inferred from fits to interparticle potentials are in good agreement with the ionic strengths inferred from conduc-

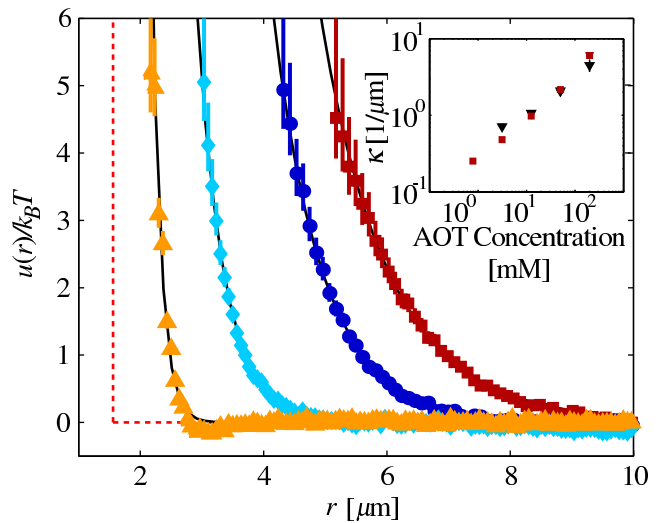


FIG. 3: Variation of interactions with [AOT]. Inferred interactions for solutions of 3, 12.5, 50 and 200 mM AOT, squares, circles, diamonds and triangles, respectively. A hard sphere potential is shown as a dashed line for comparison. Screened-Coulomb fits to each potential are plotted as solid lines. *inset* Comparison of κ as inferred from conductivity and equilibrium structure, crimson squares and black diamonds, respectively.

tivities, as shown in the inset to Fig. 3. However, the discrepancy between these two measures widens at the lowest concentration of AOT, reflecting the contributions of counterions to screening. Interestingly, we consistently observe a very small attraction in 200 mM samples. We believe that this attraction reflects the underlying structure of the reverse micelle solution, which displays a pronounced increase in viscosity at this concentration.

Our conductivity and interaction measurements show that thermodynamics is an excellent tool for predicting the concentration of ions in solution. Thermodynamics can also describe the charging of colloidal particles. In order for a particle to become charged in equilibrium, the energy cost of creating and separating surface charges and counterions must be overcome by entropy. This energy cost has three components. As we have already shown, the counterion has a solvation energy, $g_M = 12k_B T$. Similarly, an ion on the particle's surface has a solvation energy, g_S . Once the ion and counterion have been created, they must be separated at an energy cost of $e|\zeta|$, where ζ is the electrostatic potential at the surface of the particle. These costs are overcome by gains in the configurational entropy of micelles in the bulk and the configurational entropy of charges on the particle surface. When the particle charge increases by one, a neutral micelle in the bulk is converted to a charged micelle. Thus, the change in the free energy is $k_B T \ln[n_{ion}/2n_{micelle}] = k_B T \ln[\chi/2]$, where we have assumed that only a tiny fraction of micelles are charged, and that the entropies of the charged and neutral ionic

species have the same form as an ideal gas. If a particle has N chargeable sites and a charge of Z with $Z \ll N$, then the surface entropy's contribution to the chemical potential is $k_B T \ln[Z/N]$. Thus, the total chemical potential is

$$\frac{\mu}{k_B T} = g_S + g_M + \frac{e|\zeta|}{k_B T} + \ln \left[\frac{Z}{N} \right] + \ln \left[\frac{\chi}{2} \right]. \quad (4)$$

In equilibrium, $\mu = 0$. In the limit where excess ions dominate over counterions, $\chi = 2 \exp(-g_M)$, thus

$$e|\zeta| \approx -g_S - \ln[Z/N]. \quad (5)$$

Remarkably, the bulk entropic contribution to the chemical potential exactly cancels the solvation energy of the counterion. This surprising cancellation occurs because χ is pinned by the solvation energy g_M , but will break-down when a significant fraction of the charged micelles contain counterions. Consequently, the surface potential depends primarily on the competition between surface entropy and the solvation energy of an ion on the surface. However, since Z depends on the ionic strength, Eq.(2), there is some residual dependence on g_M . Since the left hand side is positive definite, meaningful results are obtained only when $-\ln[Z/N] > g_S$. Therefore, surface entropy's contribution to the chemical potential must overcome the solvation energy of the surface charge. This is in stark contrast to thermodynamic models of charging in aqueous systems, where the configurational entropy of the surface is typically ignored [18].

Combining this relation with our structural and electrokinetic measurements, we can estimate the solvation energy of a charge on the particle surface, g_S . Assuming that charges on the surface are constrained to reside within an adsorbed micelle, then packing constraints limit the number of charges to 10^6 . Our interaction measurements are consistent with $e\zeta/k_B T \approx 4$ and $Z \approx 100 - 1000$, therefore $g_S \approx 3 - 5 k_B T$, about one-quarter to one-half of the energy cost of charging an ion in bulk.

We have found that the electrostatic interactions of colloidal particles in a nonpolar solvent can be surprisingly strong and tunable. While the functional form of interparticle potentials is identical to those of charged particles in aqueous solvents, the thermodynamics of charging is qualitatively different. We expect reverse-micelle mediated colloidal interactions to play an important role in the stability and structure of new colloidal systems and to enable the exploration of fundamental physical phenomena in previously unattainable regimes. Moreover, our framework may help to illuminate the origin and consequences of charging in technologically relevant nonpolar systems.

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